Electrocatalytic properties of platinum and it's binary alloy with vanadium in oxygen reduction reaction(ORR)

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ABSTRACT

The electrocatalysis of the oxygen reduction reaction (ORR) on carbon supported Pt-V (1:1) catalyst in polymer electrolyte fuel cells (PEFC) was investigated. At an oxygen pressure of one atm an enhanced electrocatalytic property of Pt-V/C compared with Pt/C is revealed. These results indicate the occurrence of a different electrocatalytic mechanism for the ORR on Pt/C and Pt-V/C. An increase of mass transport overpotentials is observed for the Pt-V/C catalyst, and this was related to the presence of vanadium oxide. So the ORR activity of Pt-V/C at oxygen pressure of one atm is higher than that of Pt/C.

Keywords : Oxygen reduction reaction ; Platinum- Vanadium alloy;Gas diffusion-electrode ; Polymer electrolyte membrane fuel cell (PEMFC)

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INTRODUCTION

Significant progress was made during the last ten years regarding the commercialisation of fuel cells [1-3]. However, one major challenge still remaining is the large overvoltage of the oxygen reduction at the cathode, leading to a significant loss of efficiency of the fuel cell system[4-6].

This loss is even worse in direct methanol fuel cells (DMFCs), where methanol permeation from the anode to the cathode leads to depolarisation of the latter [7-9]. Therefore, there are more basic researches, are carring out to develope the catalysts used for oxygen reduction in fuel cells [10-13].

During the last decade, research has focussed on the development of two novel types of catalysts: catalysts based on heat treated, carbon-supported iron or cobalt compounds, whose active centres most probably consist of single metal centres co-ordinated by nitrogen and carbon [14–16]. Another route concerns the preparation of carbon supported transition-metal nanoparticles (mainly ruthenium and vanadium), the surface of which is modified by chalcogen (for example, selenium) or cluster-like structures [17–22]. Studying the electrochemical behaviour of Ru/Se/C and Ru/C catalysts, revealed that carbon supported ruthenium nanoparticles without chalcogen also catalyses the electro-reduction of oxygen [23–33], In this research we have focused on vanadium as an effective cocatalyst for platinium in oxygen reduction reaction which is undersized to be considered as an alternative for technical applications.

EXPERIMENTAL

The electrodes were prepared by a combined filtration/ painting procedure [34, 37] using carbon supported Pt and Pt-V (with 1:1 Pt-V atomic ratio) catalysts (20% metal/C by E-TEK), carbon powder (Vulcan XC-72, Cabot), a carbon cloth substrate, a poly tetrafluoroethylene (PTFE) suspension and a Nafion solution (5 % w/w by Aldrich). A homogeneous water suspension of carbon and PTFE was filtered under vacuum onto the both faces of the carbon cloth to form the Gas diffusion layer of the electrodes. The

composite structure was dried, then baked for 30 min at 280 ^{0}C, and finally sintered at 350 ^{0}C for 30 min. The total mass loading for the diffusion layers of the electrodes was 3 mg cm^{-2} with 15 wt.% PTFE in all cases. To prepare the catalyst layer, a homogeneous suspension was formed from the desired amounts of the Pt/C or Pt-V/C catalyst and the Nafion solution with isopropanol as solvent. The solvent was evaporated to dryness and the material was dispersed in isopropanol to form an ink, which was quantitatively deposited, on one of the faces of the composite diffusion layer by a painting procedure. As a final step, the sample was cured at 80 ^{0}C for 1 h. The metal (Pt- V) loading was 0.4 mg cm^{-2}, and the Nafion loading was 1.1 mg cm^{-2} for all electrodes. Membrane and electrodes assemblies (MEAs) were made using the procedure previously reported in references [35-38]. A Nafion 115 membrane was used. A cathode and an anode were hot pressed onto the Nafion membrane at 125 ^{0}C under a pressure of 50 MPa for 2 min. The studies were carried out in single cells (5 cm^2 of active geometric area)

and the reactant gases were externally humidified using temperature controlled humidification bottles. Testings of the single cells were conducted in a specially designed test station, measuring the cell voltage as a function of the current density.

RESULTS AND DISCUSSION

Fig. 1 shows the H$_2$/O$_2$ Polymer Electrolyte Membrane Fuel Cell (PEMFC) performance with Pt/C and Pt-V/C electrocatalysts for the ORR with same metal loading 0.4 mg cm^{-2} at 85 ^{0}C and at oxygen pressures of one atm. An increasing tendency to reach limiting diffusional currents for the electrodes with the Pt-V/C catalyst is observed and shown in Fig. 1.

In Fig. 2, the cathodic currents in modified glassy carbon electrode are obtained by cyclic voltammetery for oxygen reduction is shown for Pt/C and Pt-V/C electrocatalysts. As can be seen in the diagrams, the cathodic current for Pt-V/C electrocatalyst is higher than that of Pt/C.

In table 1, the electrochemically active surface area, as obtained by XRD

analysis is shown. In the Pt-V/C catalyst two counteracting factors affect the electrocatalytic activity, (a) the presence of unalloyed vanadium metal and its oxide decreases the active area and thus the electrocatalytic activity; and (b) the formation of real Pt-V alloy, which affect the Pt- Pt distance and the d-band vacancy, and increases the Pt electroactivity.

CONCLUSION

By comparing the fuel cell test Results ,

XRD analysis and cyclic voltammetery experiments for the two types of electrocatalysts, it is shown that binary alloy of platinium and vanadium, supported on carbon substrate (Pt-V/ C) is an effective electrocatalyst for preparing electrodes in PEMFCs applications and is a good candidate for commercialization in future.

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